



Processing, Properties and Arc Jet Testing of HfB_2/SiC

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Outline



- Background on UHTCs
- Summary UHTC Processing
 - Powder Processing
 - Scale-up
 - 2" dia. X 2" tall billets
 - 3" dia. x 2" tall billet
- Preliminary Material Properties
 - Mechanical
 - Thermal
- Arc Jet Testing
 - Flat Face Models
 - Cone Models
- Summary
- Future Work





Development of Ultra High Temperature Ceramics



- UHTCs are a family of ceramic materials, including diborides of Hf and Zr, with extremely high melting temperatures
- Previous studies have indicated good oxidation resistance in simulated reentry environments
 - ManLabs 1960's and 1970's
 - ARC 1990's
 - Ground based research: initial materials development by external vendors, Arc Jet testing, computer modeling, etc.
 - SHARP-B1(1997) and SHARP-B2 (2000) ballistic flight experiments
 - » Materials provided by external vendors
 - » Different vendors used for each flight experiment
 - » Focus on flight experiment not on materials development
 - Detailed studies still required to define use environments (Single and Multi-Use Temperatures)





Motivation for In-House Processing of UHTC Materials



- Until now there has been no consistent effort to develop the UHTC family of materials at NASA.
 - Development work has primarily been part of flight experiment programs.
 - SHARP-B1 and SHARP-B2
- Different vendors supplied materials for the SHARP-B1 and SHARP-B2 flight experiments.
 - NASA did not retain the knowledge on how to process these materials.
 - Therefore, each time the materials development has had to start at the beginning, evaluating material properties, etc...
- Resulted in inconsistent materials
 - Significant differences in microstructure leads to significant variability in material properties.
- Bringing the UHTC processing in-house allows the government to retain the knowledge of how to process the materials and then transfer the technology to industry for production.
 - Precedent has been set at ARC with development of tile coatings.





HfB₂-SiC

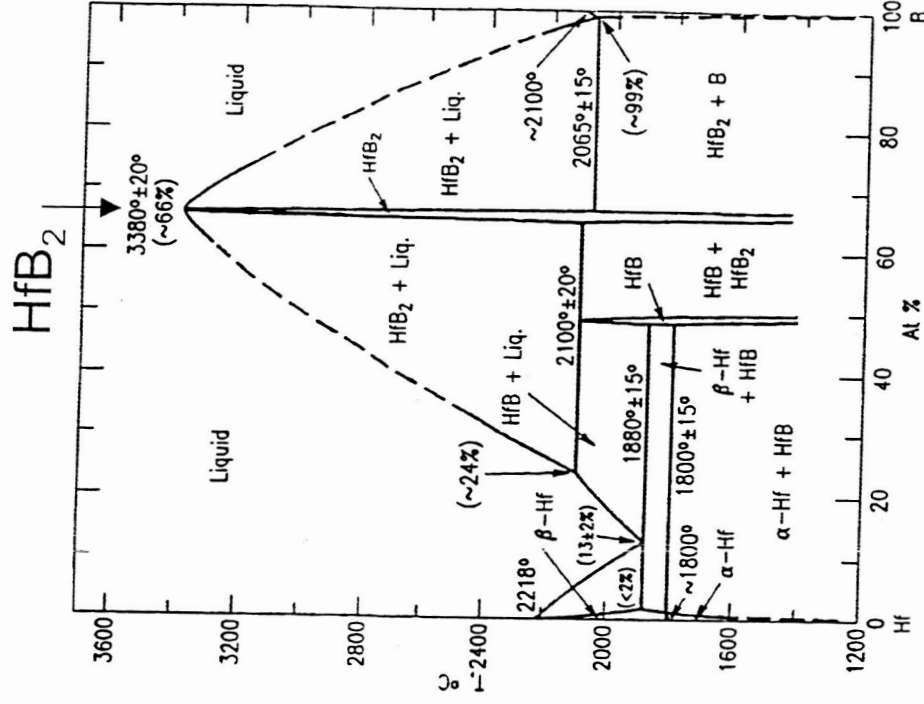


HfB₂

- HfB₂ has a narrow range of stoichiometry with a melting temperature of 3380°C
- Density = 11.2 g/cc

SiC

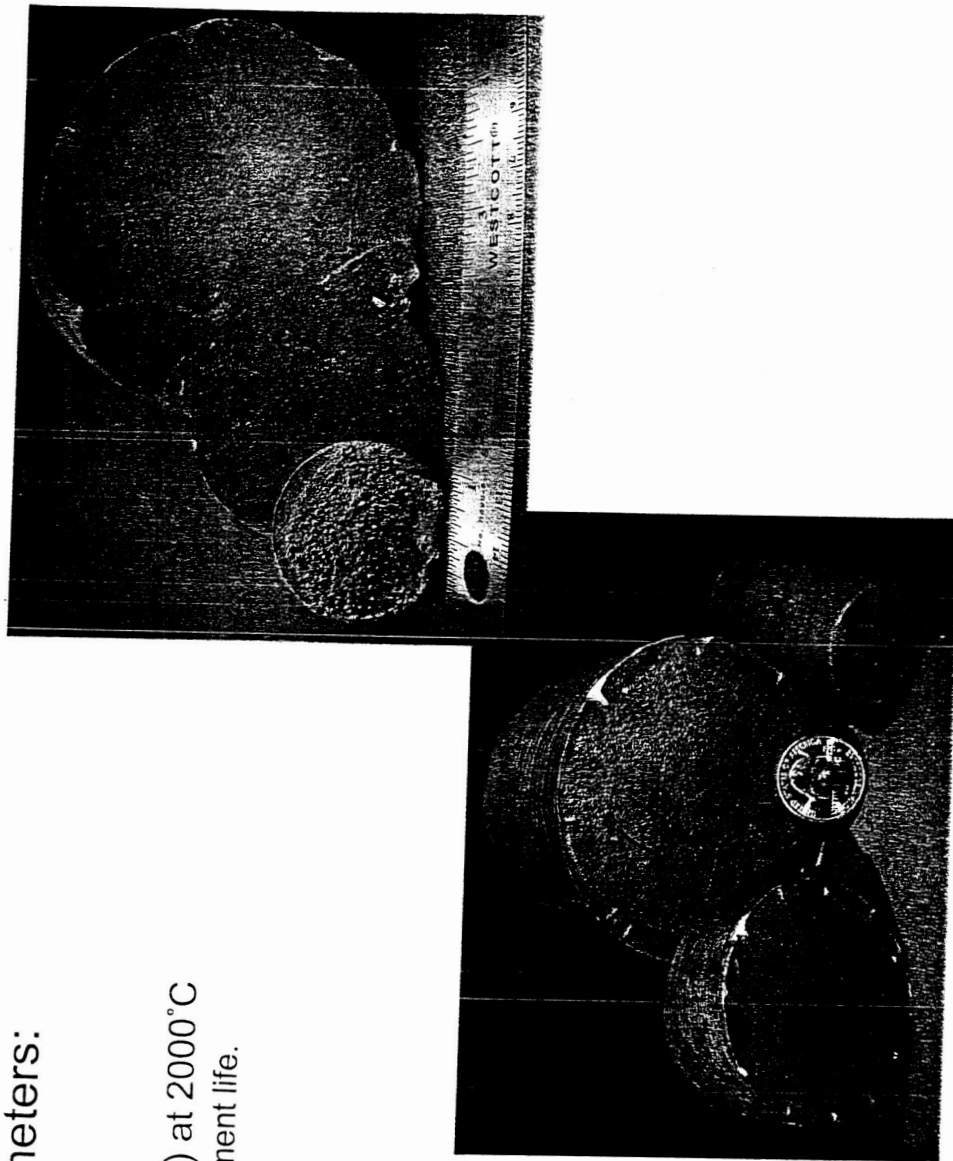
- aids densification
- limits grain growth
- may enhance oxidation resistance
- Density = 3.2 g/cc





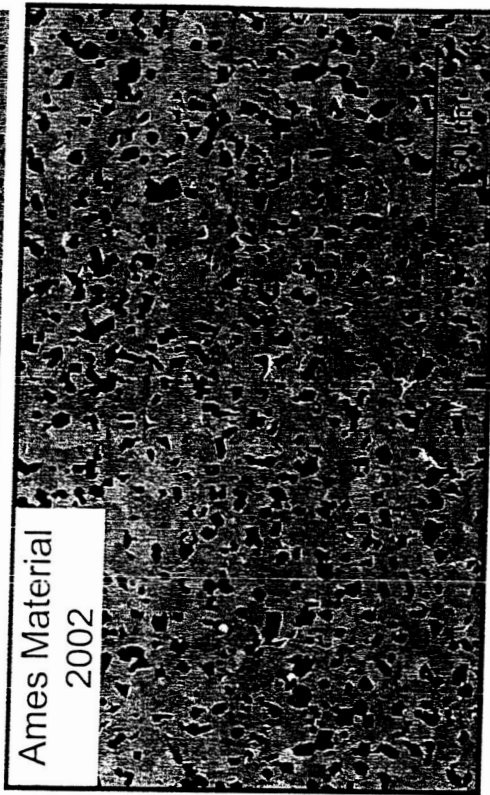
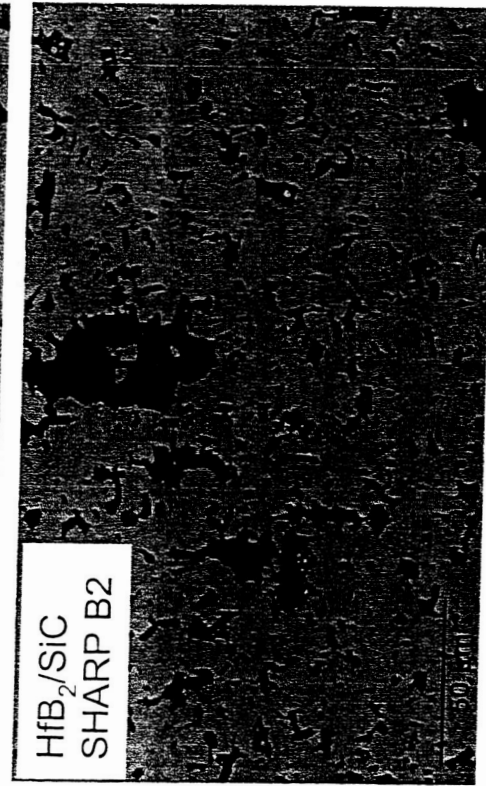
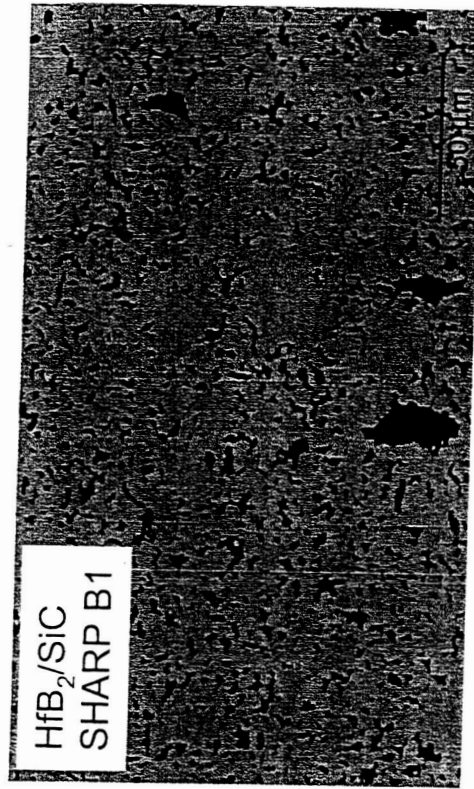
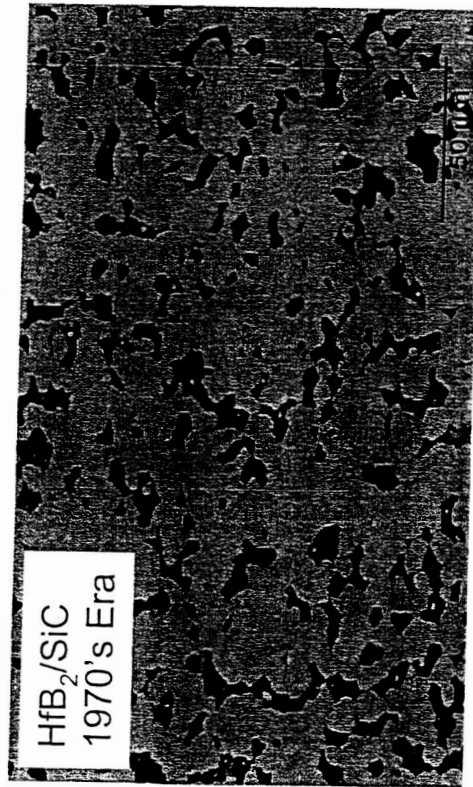
Hot Pressing

- Granulated powders are loaded into grafoil lined graphite dies
- Hot press has a graphite element with graphite insulation.
- Typical hot pressing parameters:
 - Atmosphere
 - Initially vacuum
 - Switch to inert (Ar or He) at 2000°C
 - Extends graphite element life.
 - Temperatures
 - 2000°C to 2200°C
 - Pressures
 - 3 to 4 ksi
- 67 billets pressed to date
 - (8) 2" dia. x 2" tall billets
 - (1) 3" dia. x 2" tall billet





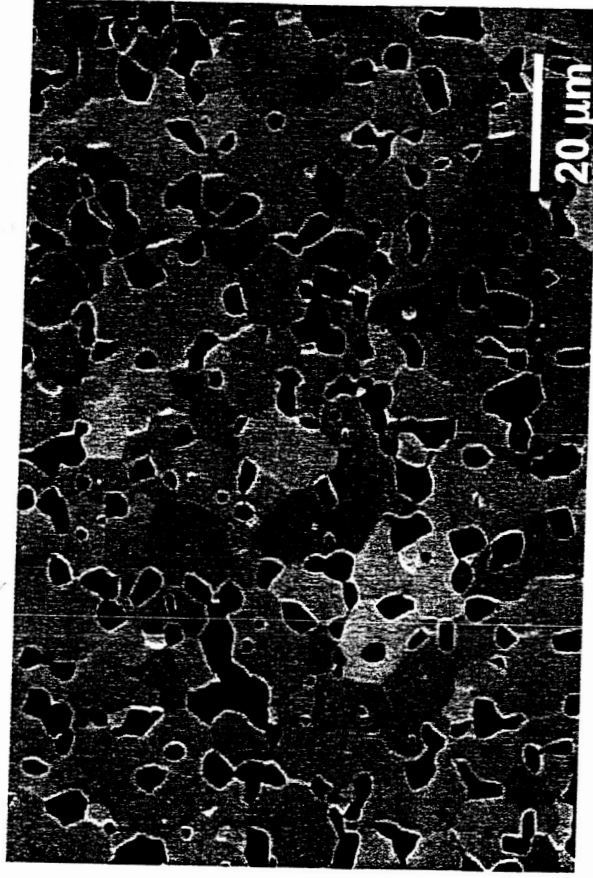
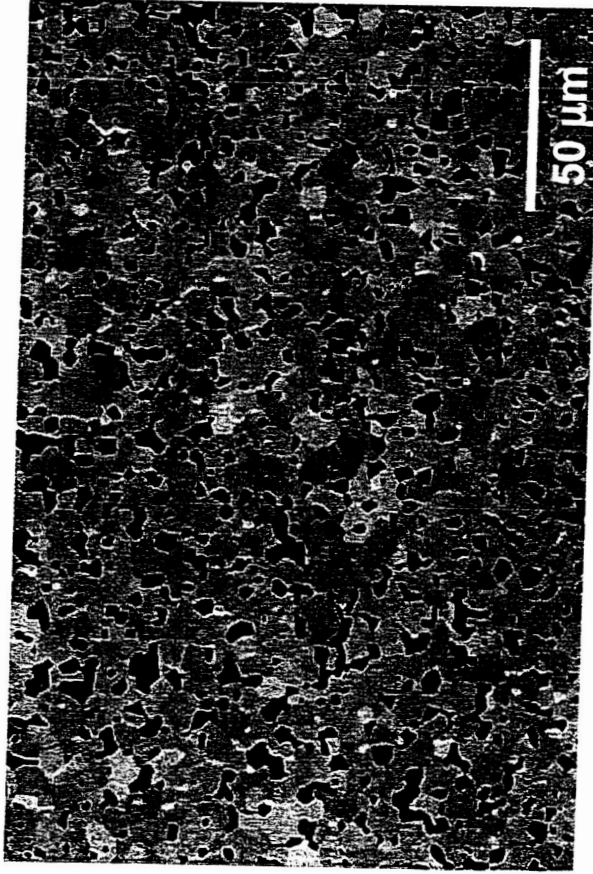
Improved Powder Handling Results In More Uniform UHTC Microstructures



- Improved powder handling eliminates SiC and HfB₂ agglomeration common in previous materials.



Microstructures of Current HfB₂-SiC Materials

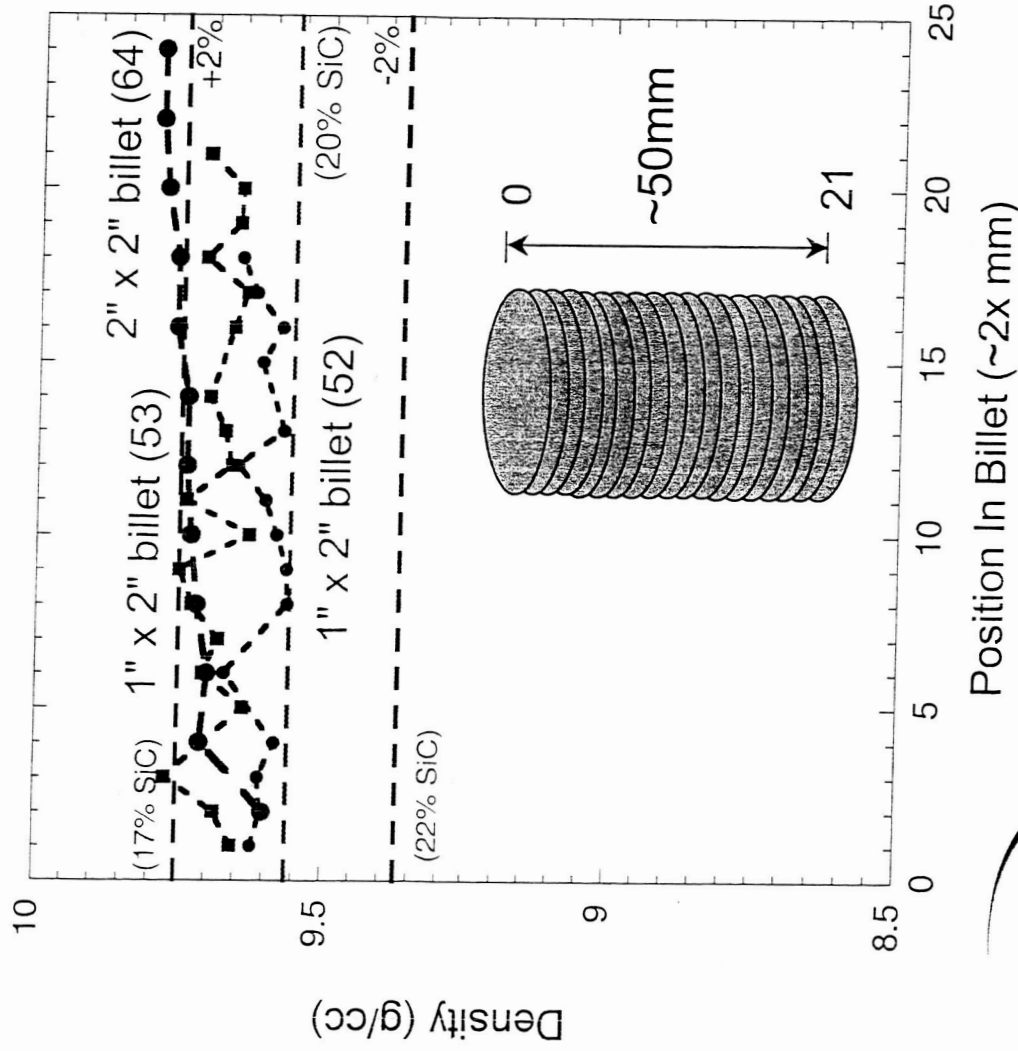


- Microstructures show uniform distribution of SiC with a relatively fine grain size.
- XRD and EDS spectra do not reveal the presence of oxide containing phases





2" Diameter Billet Has a Slightly Larger Density Gradient than the 1" Diameter Billets

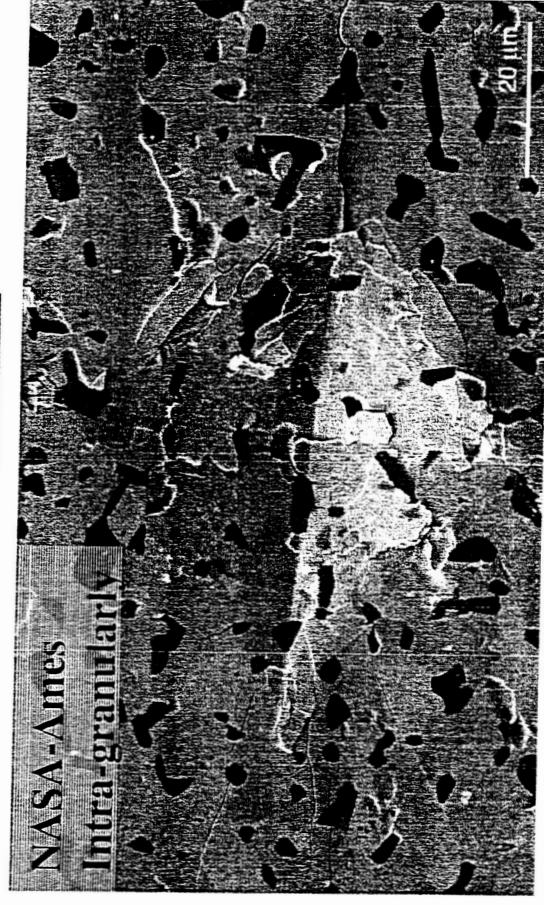
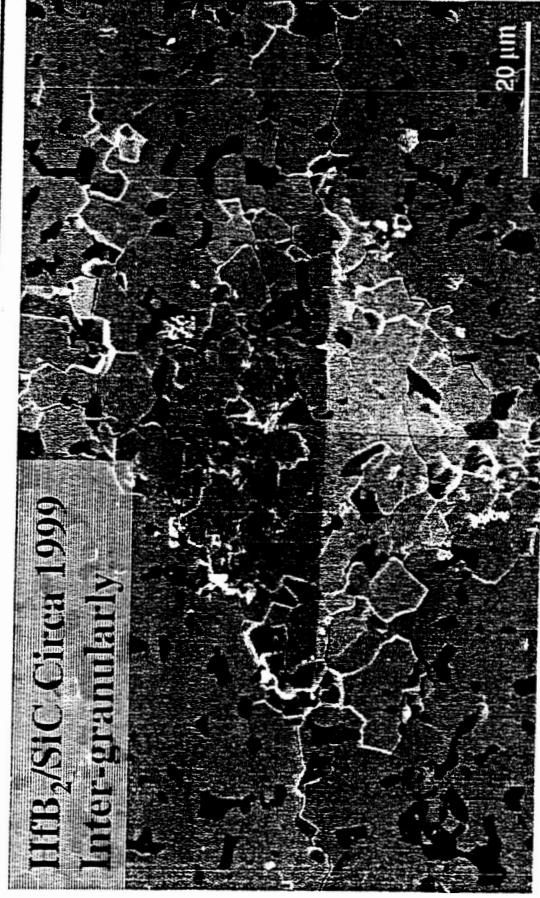


- Hot pressing schedule has not been optimized for billet scale-up.
- Densities are typically higher than theoretical due to loss of SiC during hot pressing.
- Die packing currently performed by hand, likely to result in density gradients within the powder during die packing
- Iso-static pressing of the powder, prior to die packing should increase density uniformity within powder pack increasing final hot pressed density uniformity and we should have this capability soon.





Previous HfB_2/SiC Materials and Ames HfB_2/SiC Have Comparable Hardness



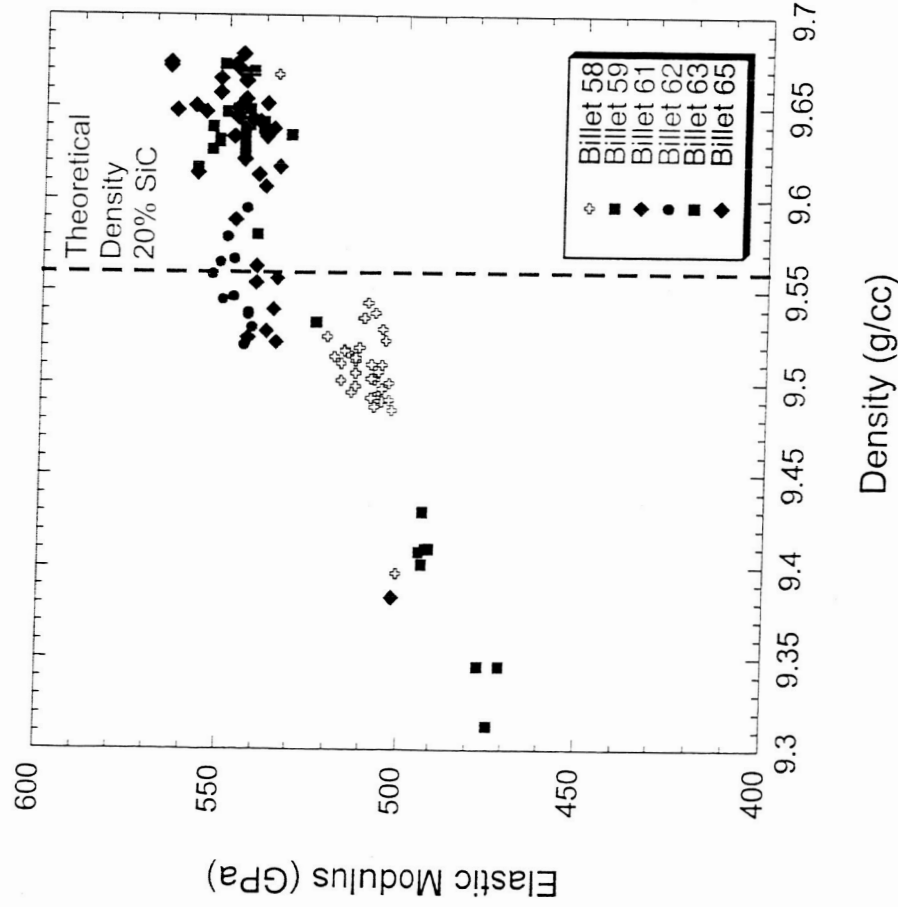
Sample ID	Vickers Hardness(GPa)	Standard Deviation
Ames Material	19.9	0.9
Circa 1999	21.2	1.0

- Cracks from indent in Ames material propagate intra-granularly (through the grains) where as in the heritage materials cracks propagated inter-granularly (between the grains).





Recent Billets Have Consistent Elastic Moduli



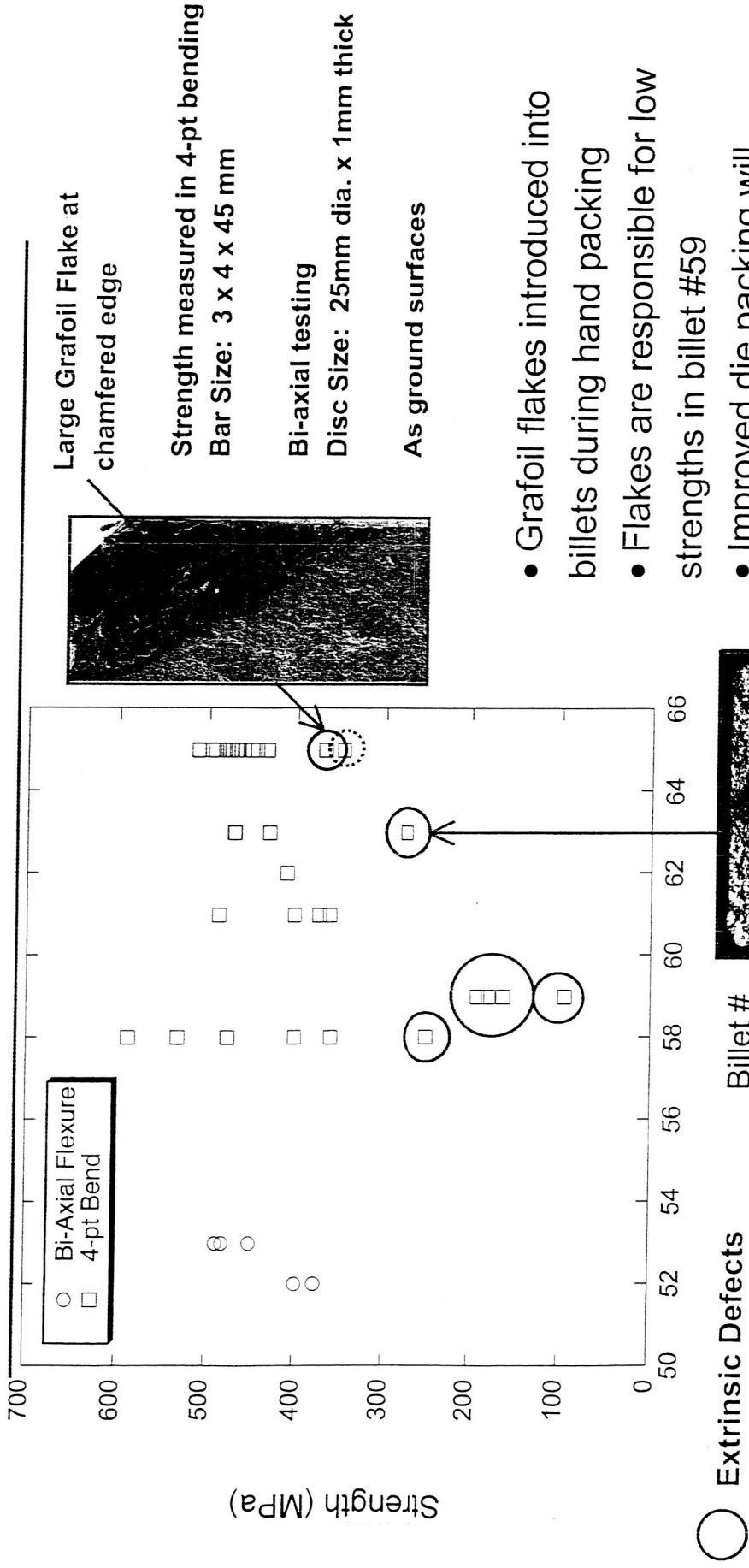
Billet #	Elastic Modulus (GPa)	# of Bars Tested
58	510 ± 9	37
59	490 ± 17	9
61	536 ± 10	10
62	547 ± 4	11
63	546 ± 6	19
65	549 ± 9	24

- Modulus decreases with decrease in density
- Decreased moduli probably due to a combination of porosity and change in SiC content (↑ SiC)
- Modulus measured using a pulse echo technique





Improved Processing Reduces Strength Distribution in Later Billets



Large Grafoil Flake at chamfered edge

Strength measured in 4-pt bending
Bar Size: 3 x 4 x 45 mm

Bi-axial testing

Disc Size: 25mm dia. x 1mm thick

As ground surfaces

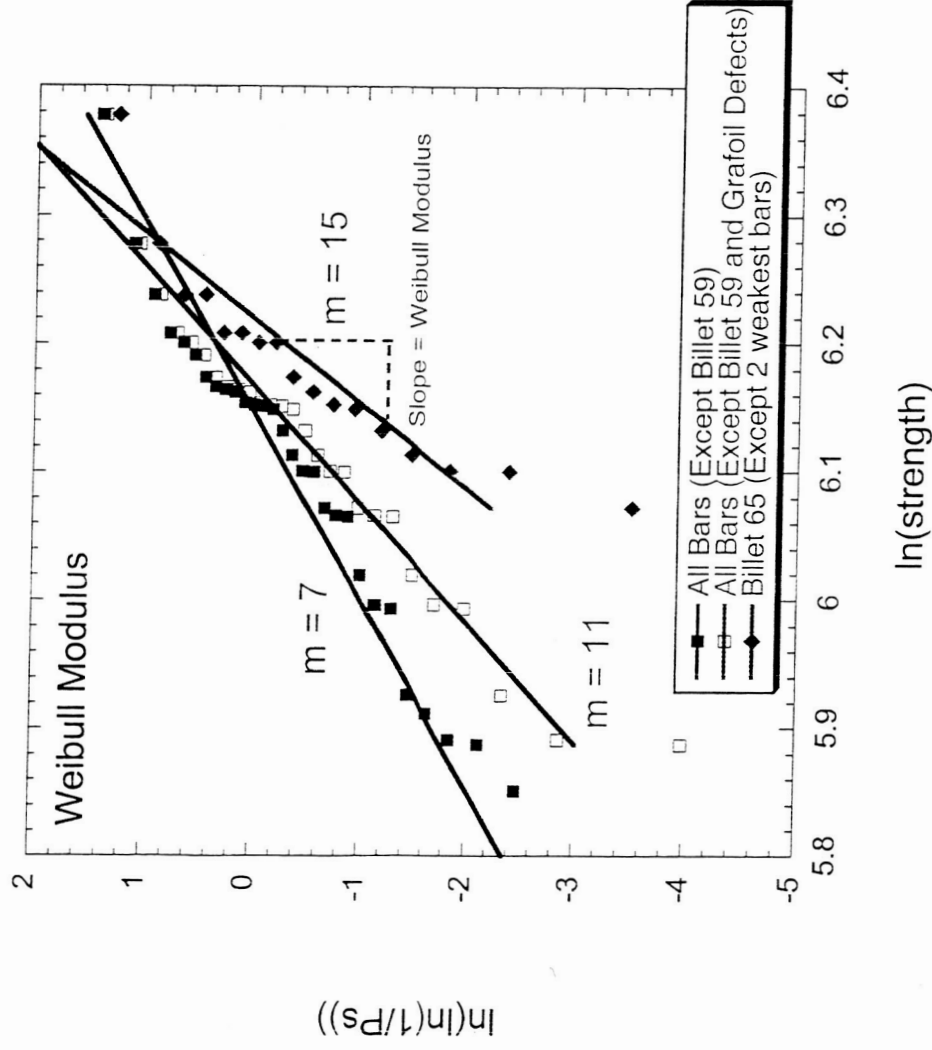
- Grafoil flakes introduced into billets during hand packing
- Flakes are responsible for low strengths in billet #59
- Improved die packing will eliminate this source of extrinsic defects

ASTM C1161





Weibull Modulus of ARC HfB₂/SiC Improved Compared to Previous Materials



- Strength distributions are improving with time, as experience is gained.



Weibull Modulus of previous materials (1999 era) ~4.



Summary of Strengths

Billet #	Strength (MPa)	# of Bars Tested	Strength Less Extrinsic Defects (MPa)
58	440 ± 114	7	473 ± 89 (6)
59	157 ± 43	4	
61	407 ± 57	4	
62	411	0	
63	415 ± 81	5	451 ± 22 (4)
65	454 ± 46	14	460 ± 41 (13) 470 ± 23 (12)*
SHARP B2	356 ± 91	30	
ManLabs	312 ± 26	3	

• For this average and standard deviation assumed that both low strength bars in billet 65 had an extrinsic defect such as grafoil, fractography has confirmed this for one bar, continuing examination of other bars.



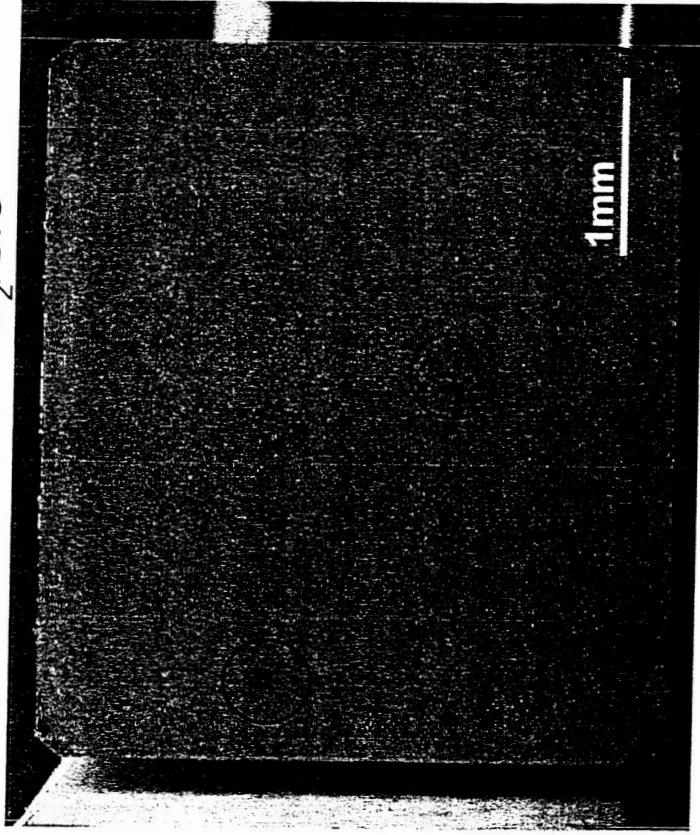
• All strengths measured in 4-pt bending on 3 x 4 x 45 mm bars



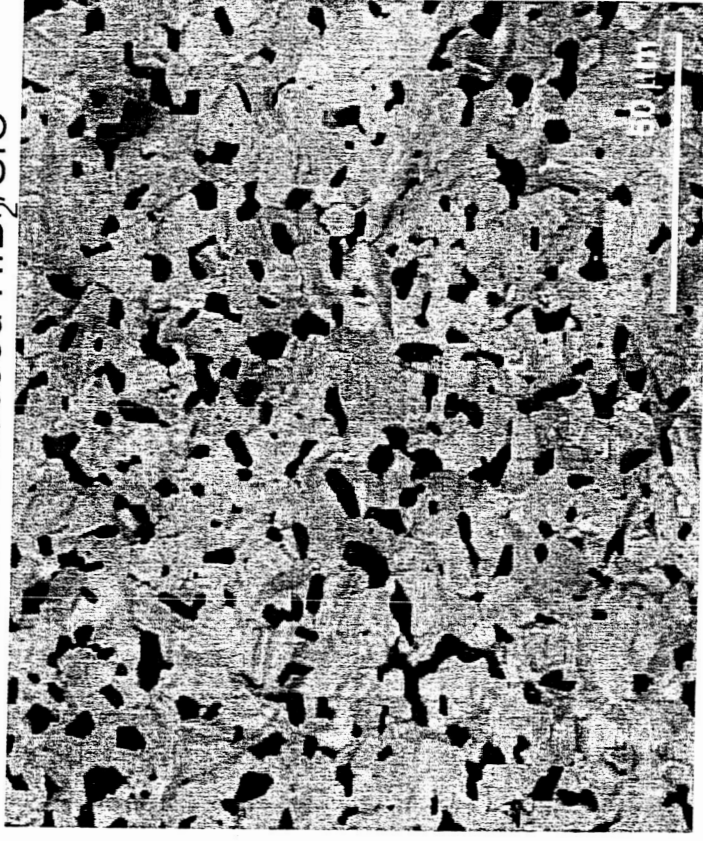
Fracture Surfaces of ARC Materials Do Not Show Evidence of SiC Agglomeration



Circa 1999 HfB₂/SiC



Ames Processed HfB₂/SiC



- Red circles highlight SiC agglomerates found in SHARP B2 material as a result of un-optimized powder processing
- Fracture surfaces of ARC materials do not reveal SiC agglomeration
- Some ARC bars show Grafoil flakes in the material introduced during die packing
 - Grafoil defects can be eliminated via improved die packing procedures

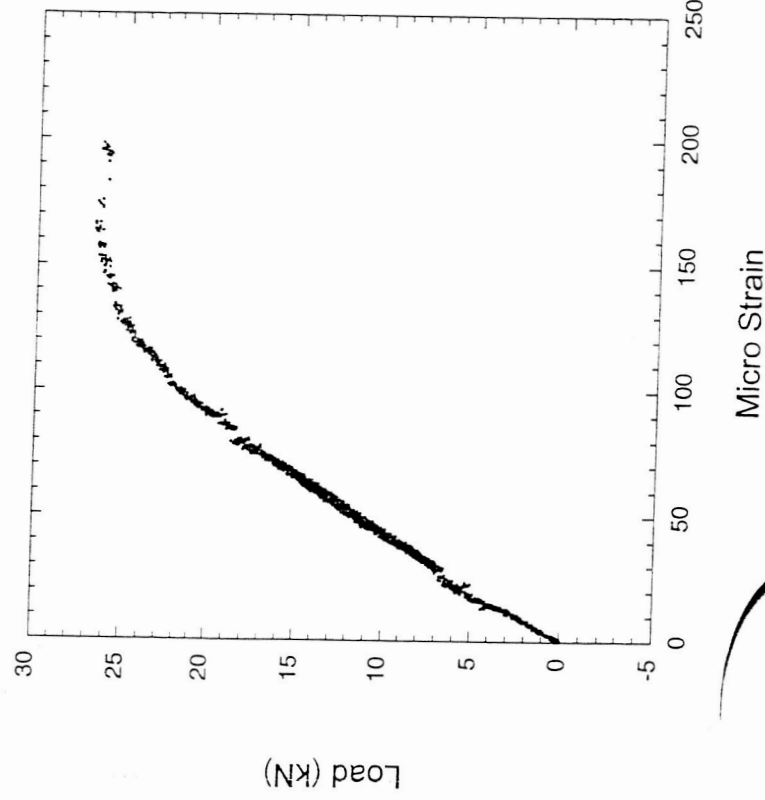




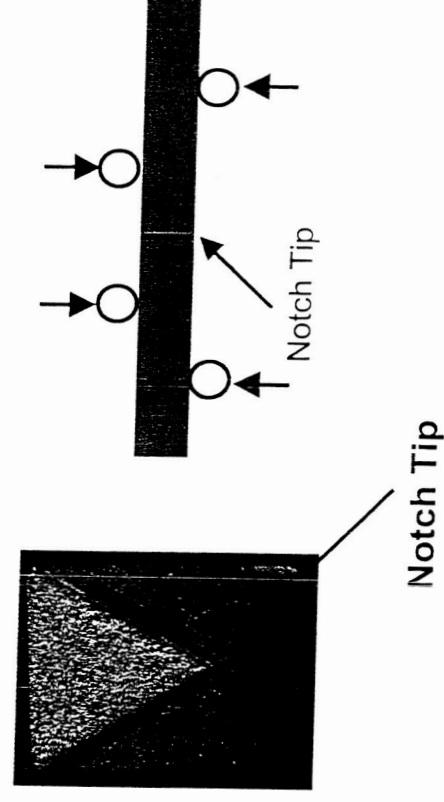
SiC Particulate Does Not Appear to Affect the Materials Fracture Toughness



- Fracture toughness measured according to ASTM C1421
- Used Chevron Notched Specimens
- Bar Size: 3 x 4 x 45 mm
- Need stable crack growth during test

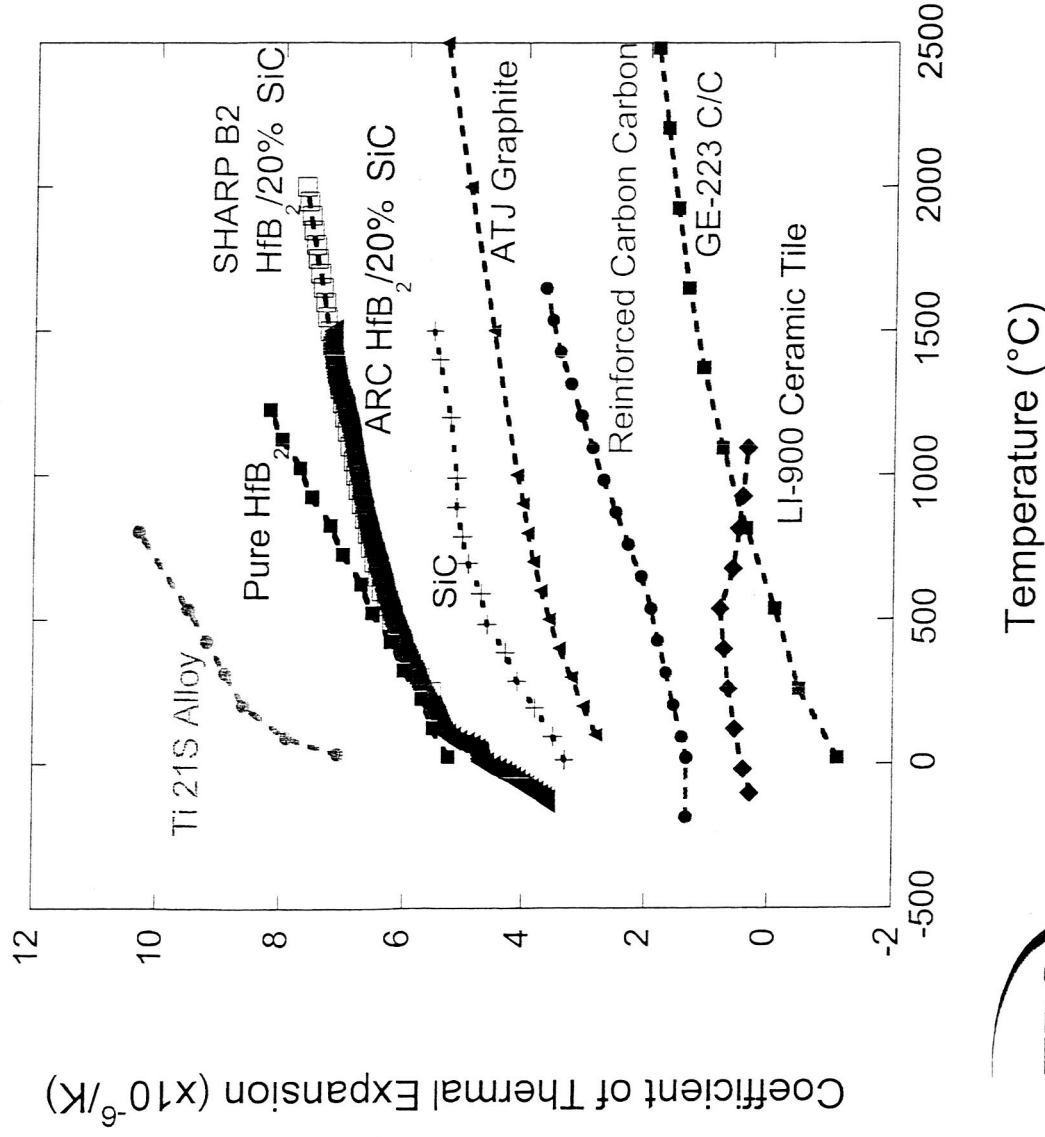


Material	K_{IVB} (MPa $m^{1/2}$)
Si_3N_4	3 - 7
Al_2O_3	3 - 4
SiC	3 - 4
Porcelain	~1
Si	~1
HfB ₂ /20% SiC	4.1 ± 0.2





CTE of ARC HfB_2/SiC is the Same as SHARP B2 Material

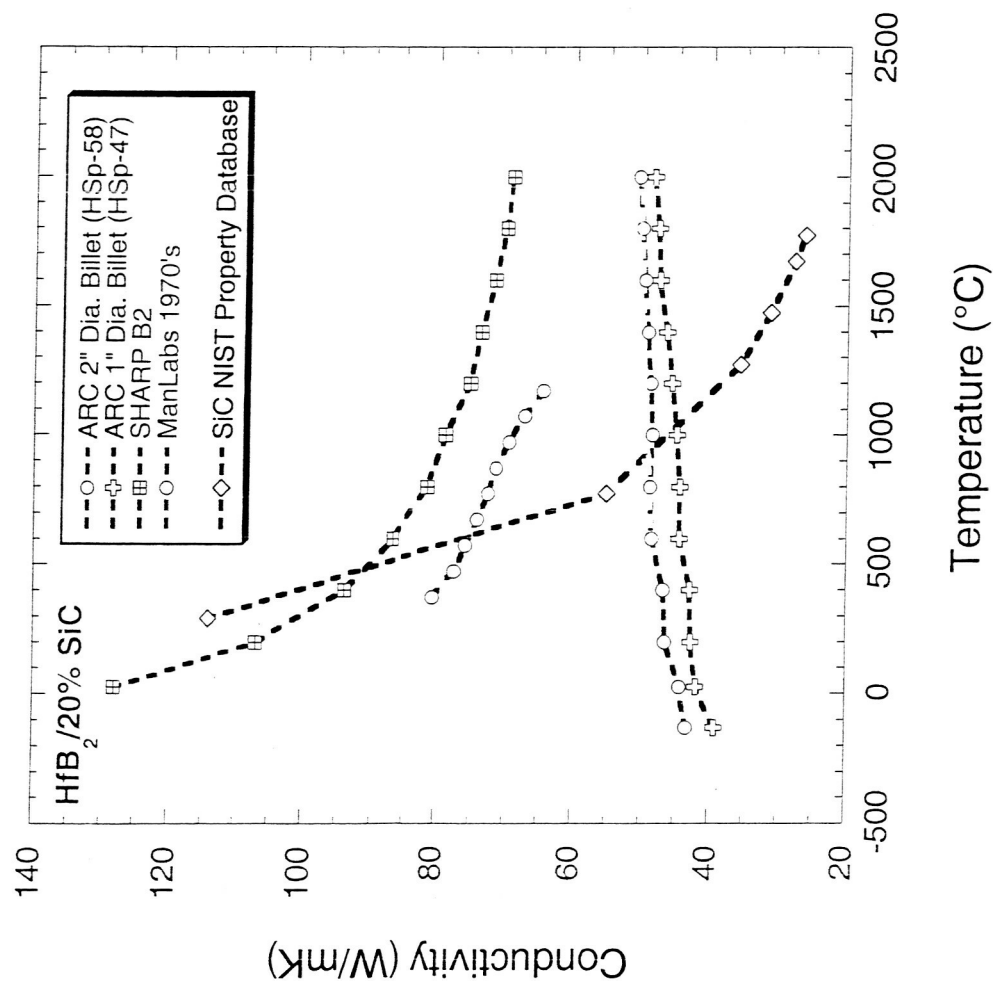


- CTE measured using high temperature dilatometry
- Pushrod dilatometer used
- $T = -130^{\circ}\text{C}$ to 1500°C





Conductivity of ARC Materials Lower than Heritage Materials





Summary: Processing and Properties



- Modified hot pressing schedule has significantly improved UHTC billet processing
 - Density and microstructure uniformity have improved
- 2" dia. x 2" tall UHTC billets have been successfully hot pressed
 - Scaled up billets have slightly higher density gradients axially than 1" billets
 - Need to evaluate radial density uniformity
 - Hot press schedule has not been optimized for scaled up billets
 - Hot pressed (1) 3" dia. x 2" tall billet
- Strengths and strength distributions are improving with experience
 - Need to evaluate strength uniformity in the center of the billets
 - Most bars cut from outside of billet around wedge models
- CTE or ARC materials compares favorably with heritage materials.
- Thermal conductivity of ARC materials considerably different than that of heritage materials.





Behavior of HfB_2 -SiC Materials in Simulated Re-Entry Environments



Thermal Protection Materials and Systems Branch



Arc Jet Testing Objectives/Goals



- Investigate the oxidation/ablation behavior of HfB_2/SiC materials in simulated re-entry environments
- Use the arc jet test results to define appropriate use environments for these materials for use in vehicle design
 - Use environments will be vehicle dependent
 - Application will drive desired performance
 - Parameters to be investigated include:
 - Surface Temperature
 - Stagnation Pressure
 - Duration
 - # of Cycles
 - Thermal Stresses

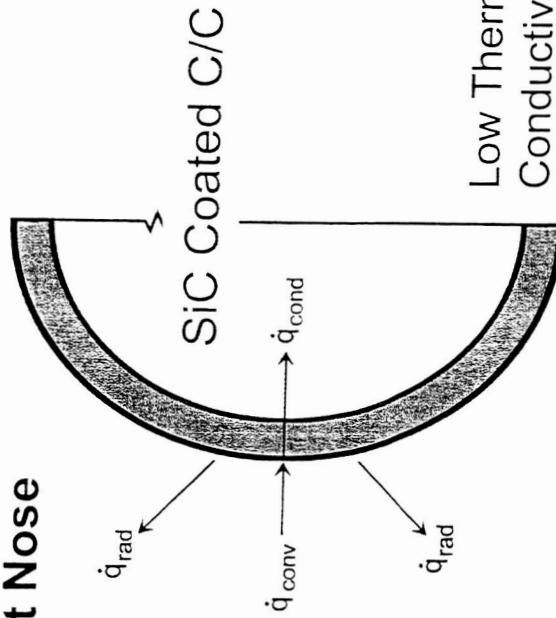




Surface Energy Balance



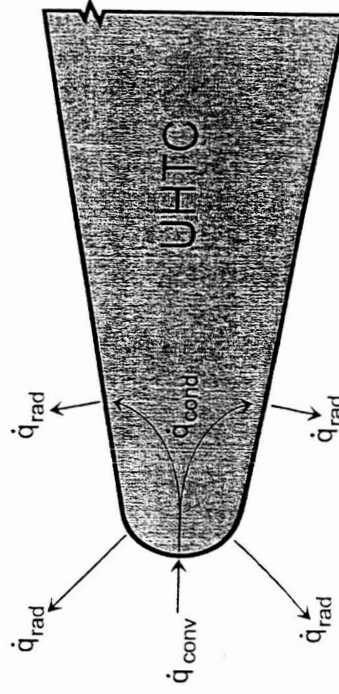
Blunt Nose



Low Thermal Conductivity
 $q_{cond} \approx 0$

$$\dot{q}_{conv} \approx \dot{q}_{rad}$$

Sharp Nose



High Thermal Conductivity

$$\dot{q}_{conv} = \dot{q}_{rad} + \dot{q}_{cond}$$

- Insulators and UHTCs manage energy in different ways:
 - Insulators store energy until it can be eliminated the same way it came in
 - UHTCs conduct energy through the material and reradiate it through cooler surfaces





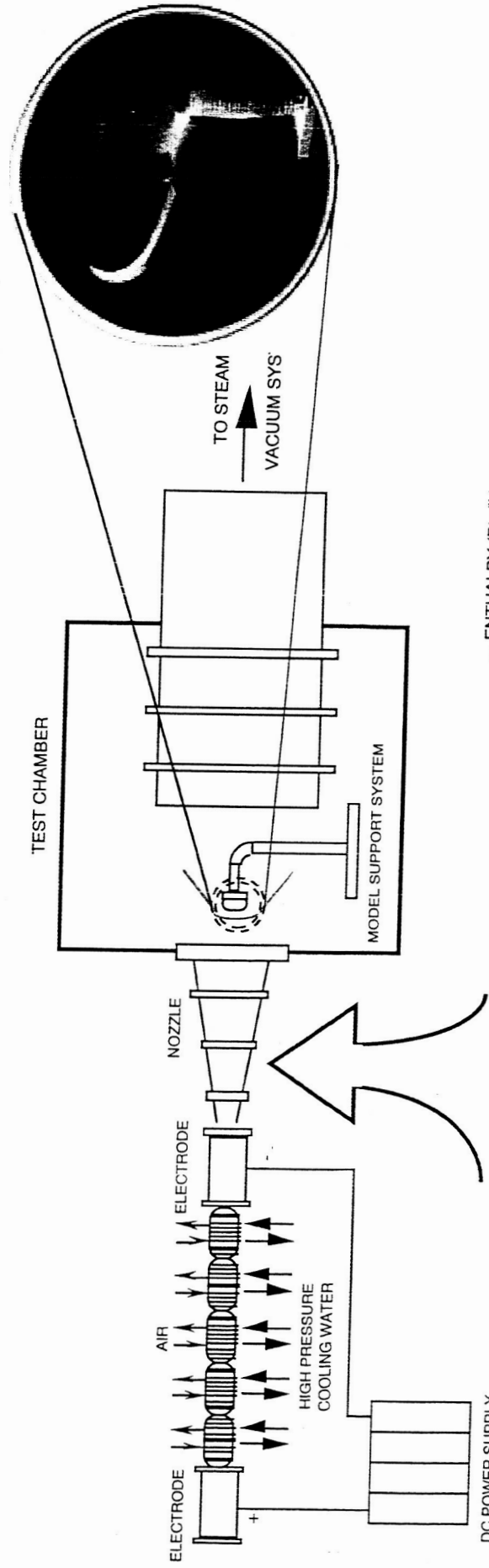
Needs for Arc Jet Testing

- Arc jet testing is the best ground based method of evaluating a materials oxidation/ablation response in re-entry environments
- A materials oxidation behavior when heated in static or flowing air at ambient pressures is likely to be significantly different than in a re-entry environment.
- In a re-entry environment:
 - Oxygen and nitrogen may be dissociated
 - Catalycity of the material plays an important role
 - Recombination of O and N atoms adds to surface heating
 - Stagnation pressures may be less than 1 atm.
 - Influence of active to passive transitions in oxidation behavior of materials
 - SiC materials show such a transition when the protective SiO_2 layer is removed as SiO

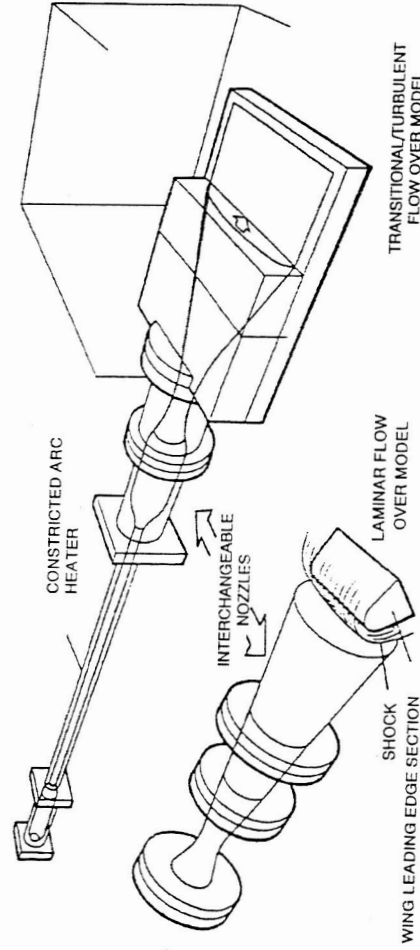




Arc Jet Testing



- ENTHALPY (Btu/lb): 4000 - 20000
- STAGNATION PRESSURE (atm):
 - FLAT-FACE MODEL 0.005 - 1.2
 - WEDGE MODEL 0.0001 - 0.15
- HEATING RATES (Btu/ft²-sec):
 - FLAT-FACE MODEL 20 - 660
 - WEDGE MODEL 0.5 - 45
- SAMPLE SIZE (ft):
 - FLAT-FACE MODEL Up to 1.5
 - WEDGE MODEL Up to 2.5 x 2.5

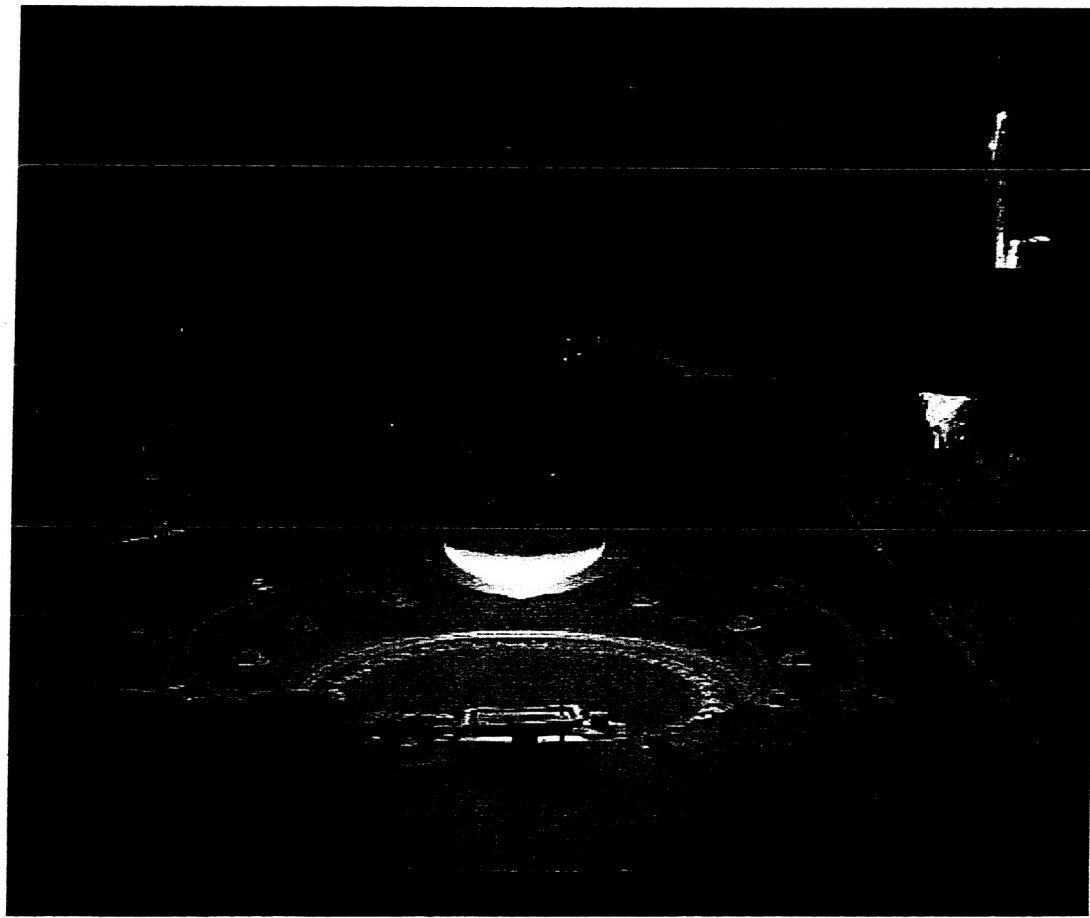


• Ground based simulation of re-entry environment.



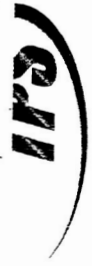
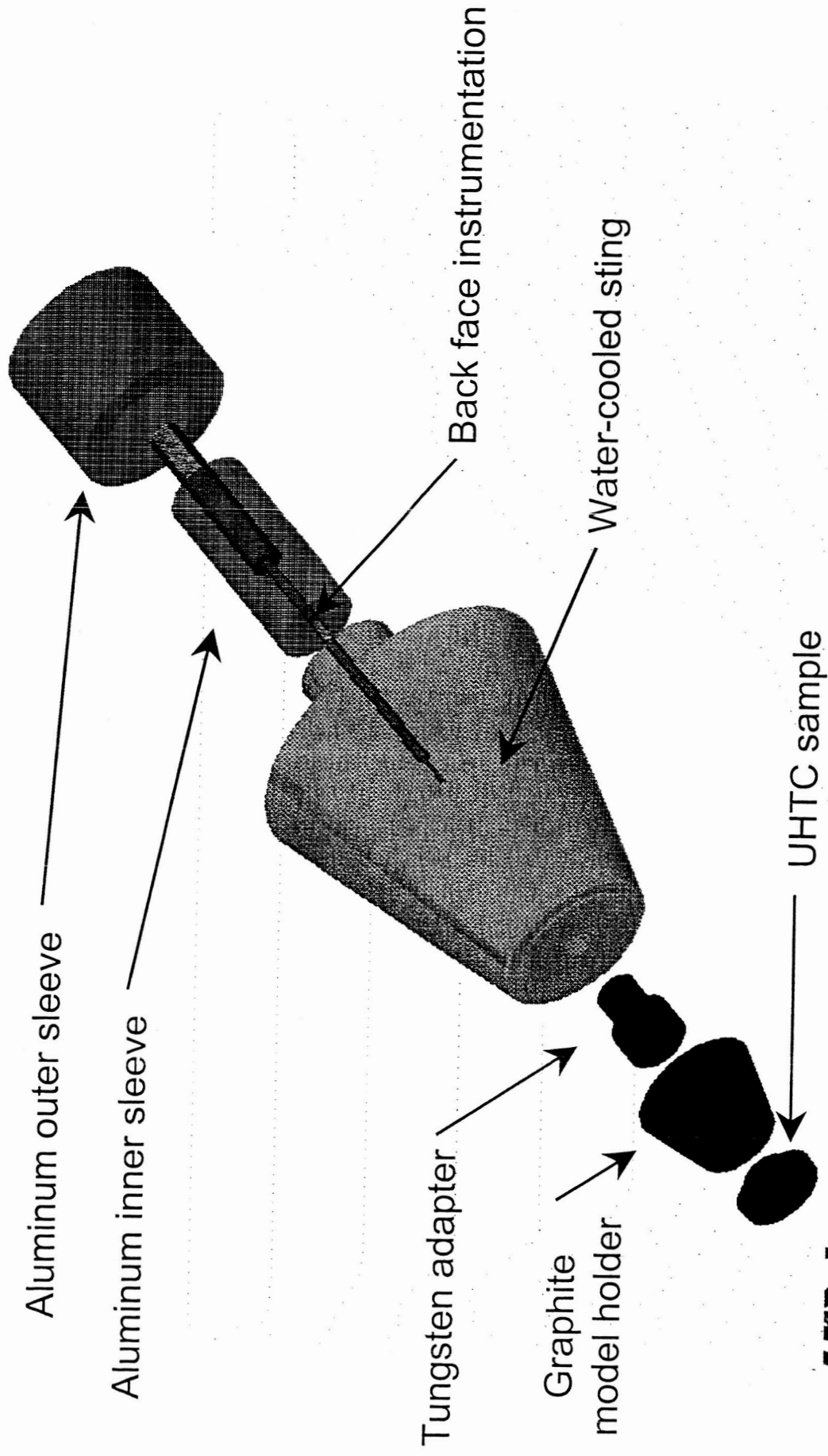


Example of Model During Arc Jet Testing



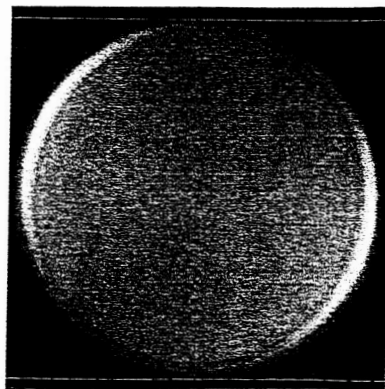


Use-Temperature (Flat Face) Model Assembly

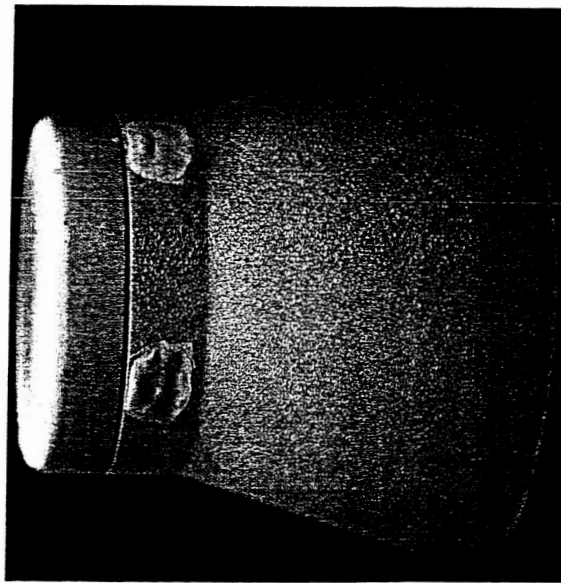




Specimen Geometry

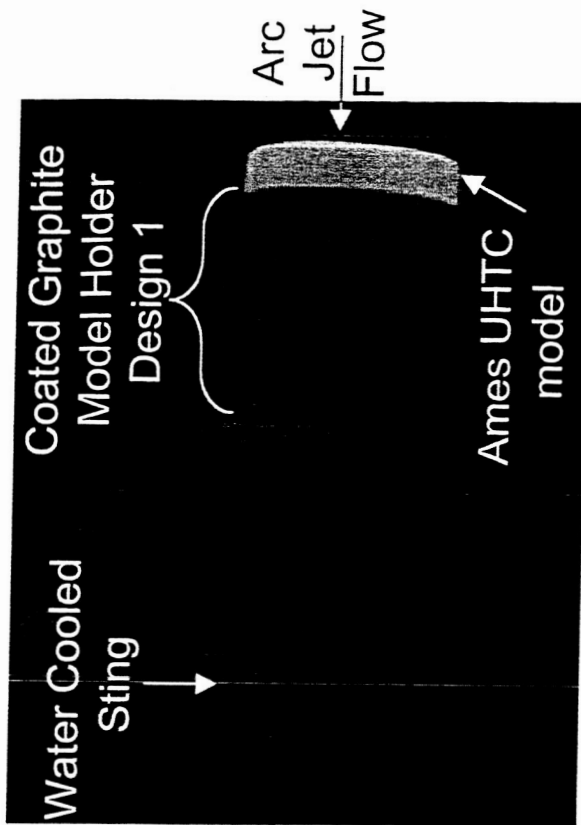


Original
Specimen



2.54 cm

Specimen mounted in
coated graphite holder
Design 1
Held by graphite pins
(ends protected)



Specimen on
Sting Arm





Arc Jet Test Conditions

Model #	Density (g/cc)	Heat Flux (W/cm ²)*	Pressure (atm)
FF-61-1	9.59	285	0.05
FF-61-2	9.57	350	0.07
FF-62-1	9.64	430	0.08
FF-62-2	9.47	530	0.11

*Heat flux is referenced to a 3" Cu hemisphere

- Each model was run twice
- Run durations were 10 min. each
- Flat face models machined from 2" dia. Billets
- Surface temperatures are measured using 1-color and 2-color optical pyrometers.



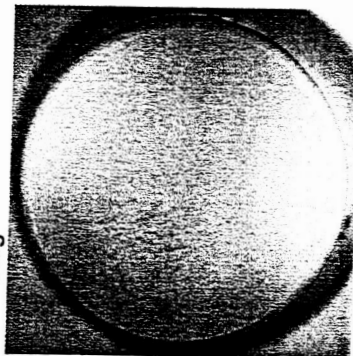


Summary of Flat Face Models



1st
Run

$q_{\text{stag}} = 285 \text{ W/cm}^2$
 $P_{\text{stag}} = 0.05 \text{ atm}$



% $\Delta \text{wt} = -0.0$

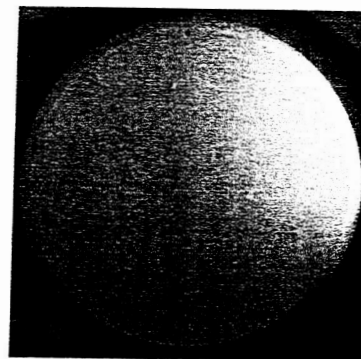
$q_{\text{stag}} = 350 \text{ W/cm}^2$
 $P_{\text{stag}} = 0.07 \text{ atm}$



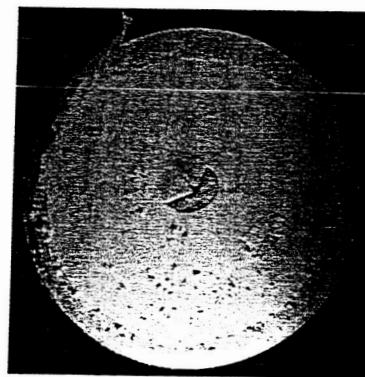
% $\Delta \text{wt} = -0.5$

2nd
Run

% $\Delta \text{wt} = -0.0$
 $T_{\text{ss}} = 1691^\circ\text{C}$

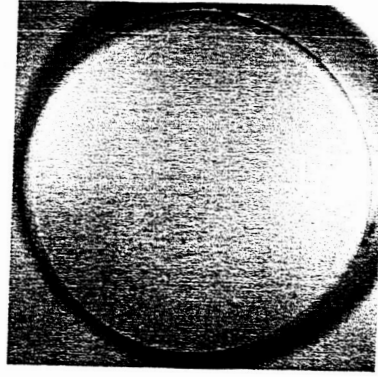
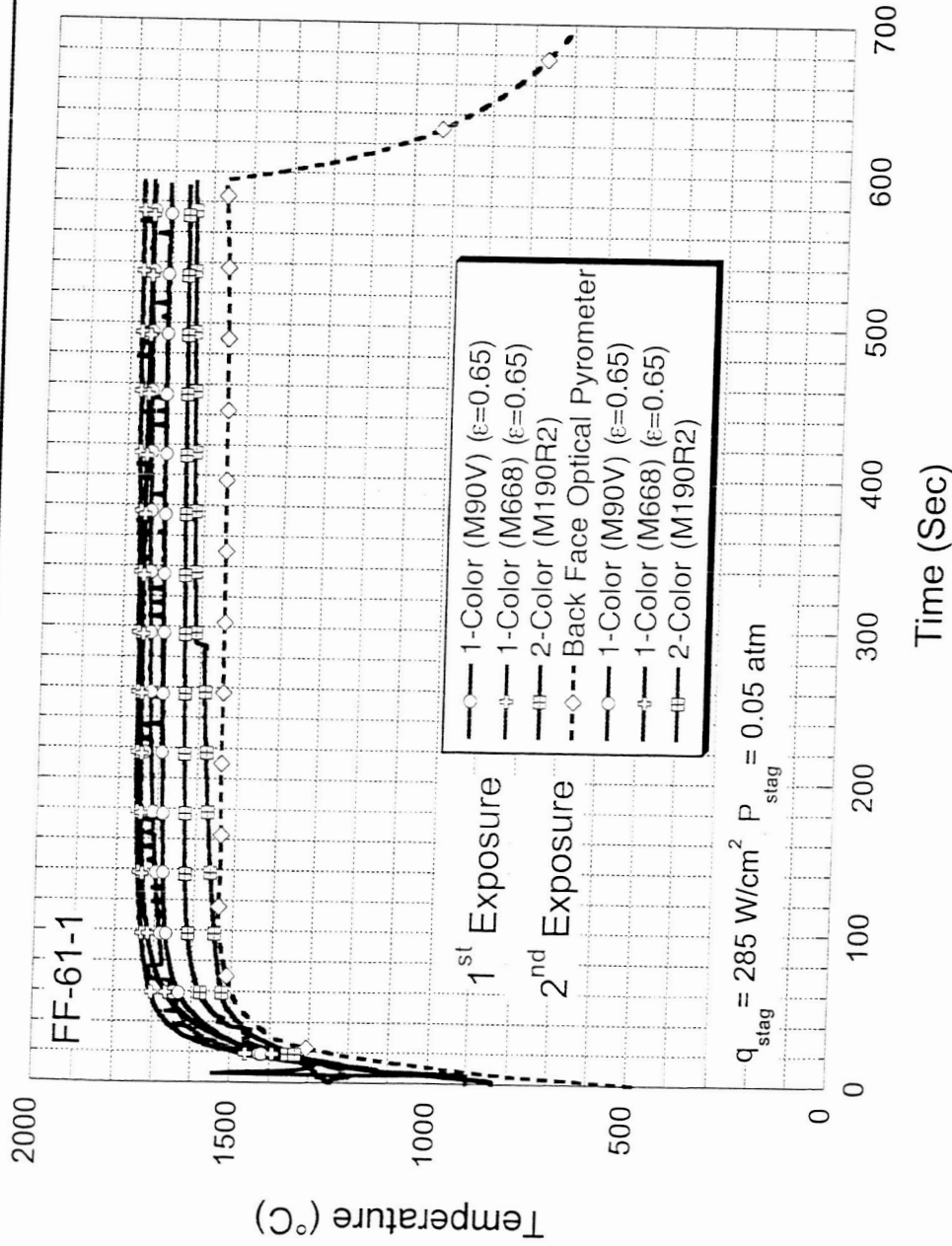


% $\Delta \text{wt} = -1.0$
 $T_{\text{ss}} = 2362^\circ\text{C}$

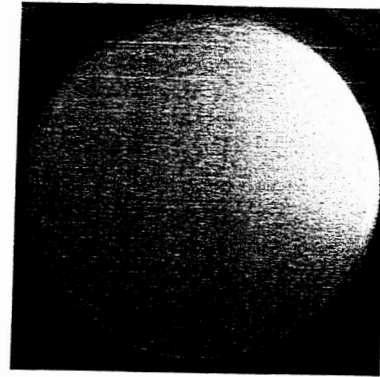




FF 61-1: $q_{\text{stag}} = 285 \text{ W/cm}^2$



1st Run



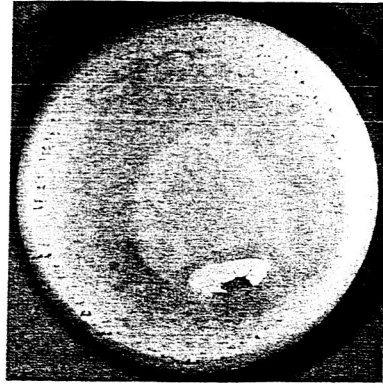
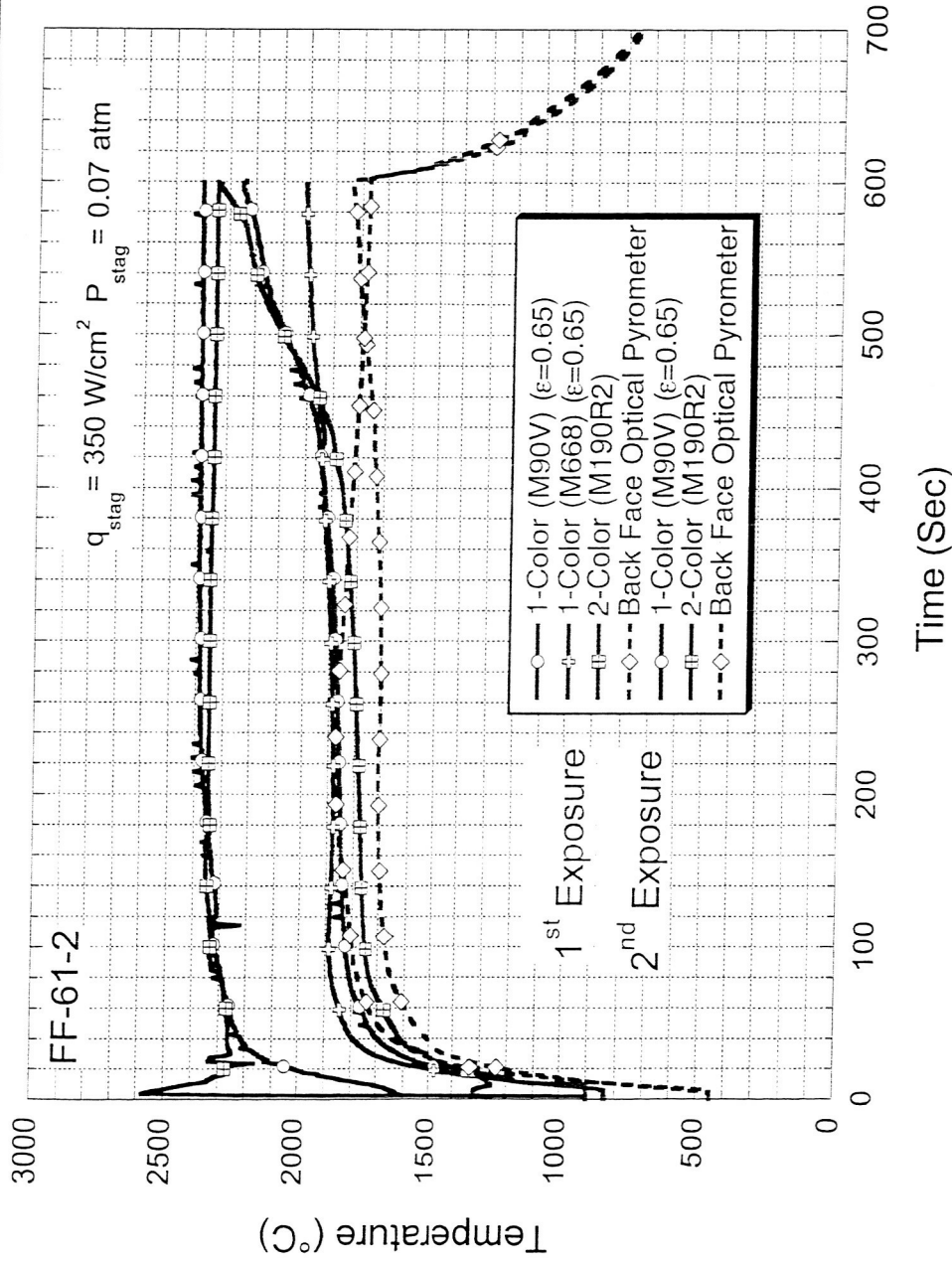
2nd Run



- Surface temp. does not change during 2nd exposure
- For the 1-color pyrometers assuming an $\epsilon = 0.65$ based on ManLabs results



FF 61-2: $q_{\text{stag}} = 350 \text{ W/cm}^2$



1st Run



2nd Run

- Surface temp. begins to rise toward end of 1st exposure
- During the 2nd exposure surface temp rises to same point where temp. peaked during the 1st exposure





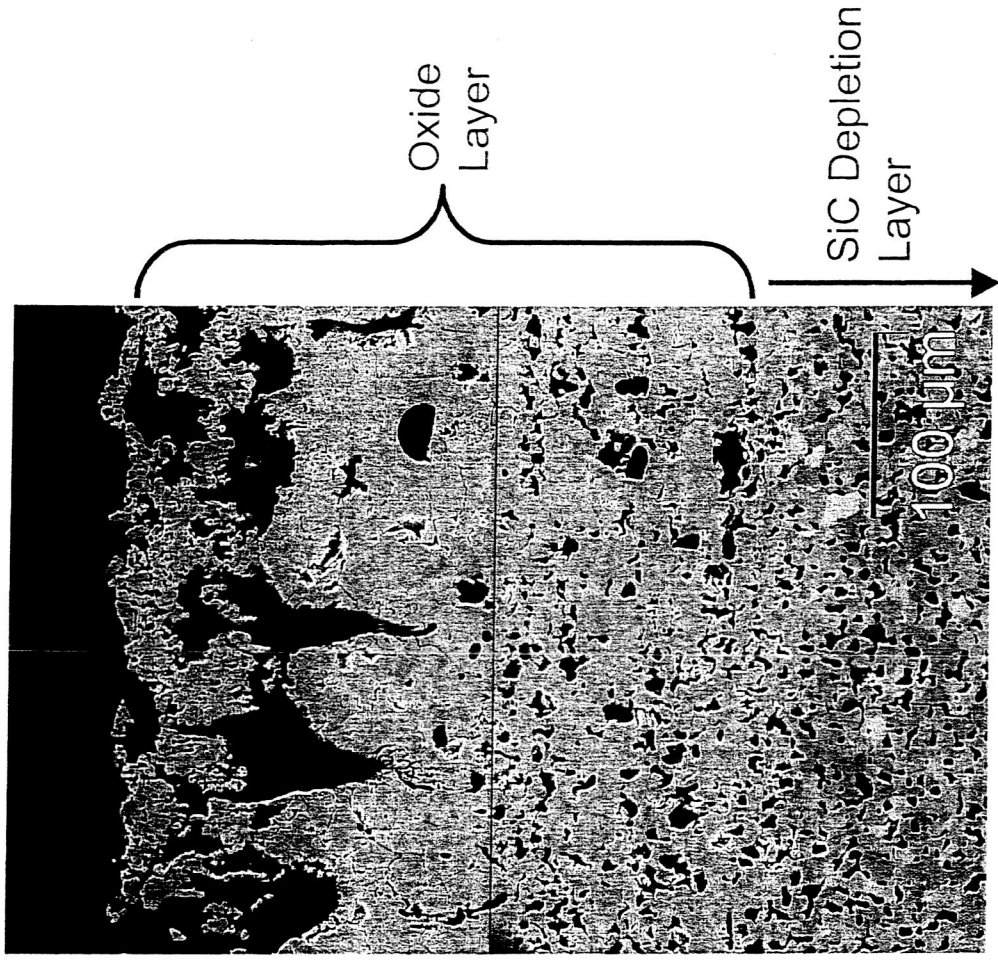
Porous Oxide Layer Forms During Arc Jet Testing



Surface of Model



Cross Section



$q_{\text{stag}} = 350 \text{ W/cm}^2$, $P_{\text{stag}} = 0.07 \text{ atm}$



Summary:



Flat Face Arc Jet Testing

- Completed testing of 4 UHTC models
 - Two 10 min. exposures each
- Surface temperatures in excess of 2300°C have been observed with some oxidation and spalling of the oxide layer, but no apparent large scale melting.
- During arc jet testing 2 zones in the material develop:
 - A surface oxide layer, primarily composed of HfO_2
 - And a porous HfB_2 region between the surface HfO_2 layer and the base HfB_2/SiC material.
- Active oxidation of the SiC results in the porous HfB_2 layer below the surface oxide layer.
- At ~20 vol. % the SiC particulate phase is above the percolation threshold and results in an interconnected SiC phase which is oxidized away and results in the depletion zone.
- The surface temperatures during the 2nd exposures at heat fluxes between 350 and 530 W/cm² are similar.





Future Work

- Perform additional arc jet testing to adequately define multi-use temperature/environment, includes evaluation of:
 - Multiple Exposures
 - Long Durations
 - Different Stagnation Pressures
- Use experimental results to develop models to describe the oxidation mechanisms and use for predictions
- Investigate alternative compositions
 - Different SiC contents
 - Different additives
 - ZrB_2





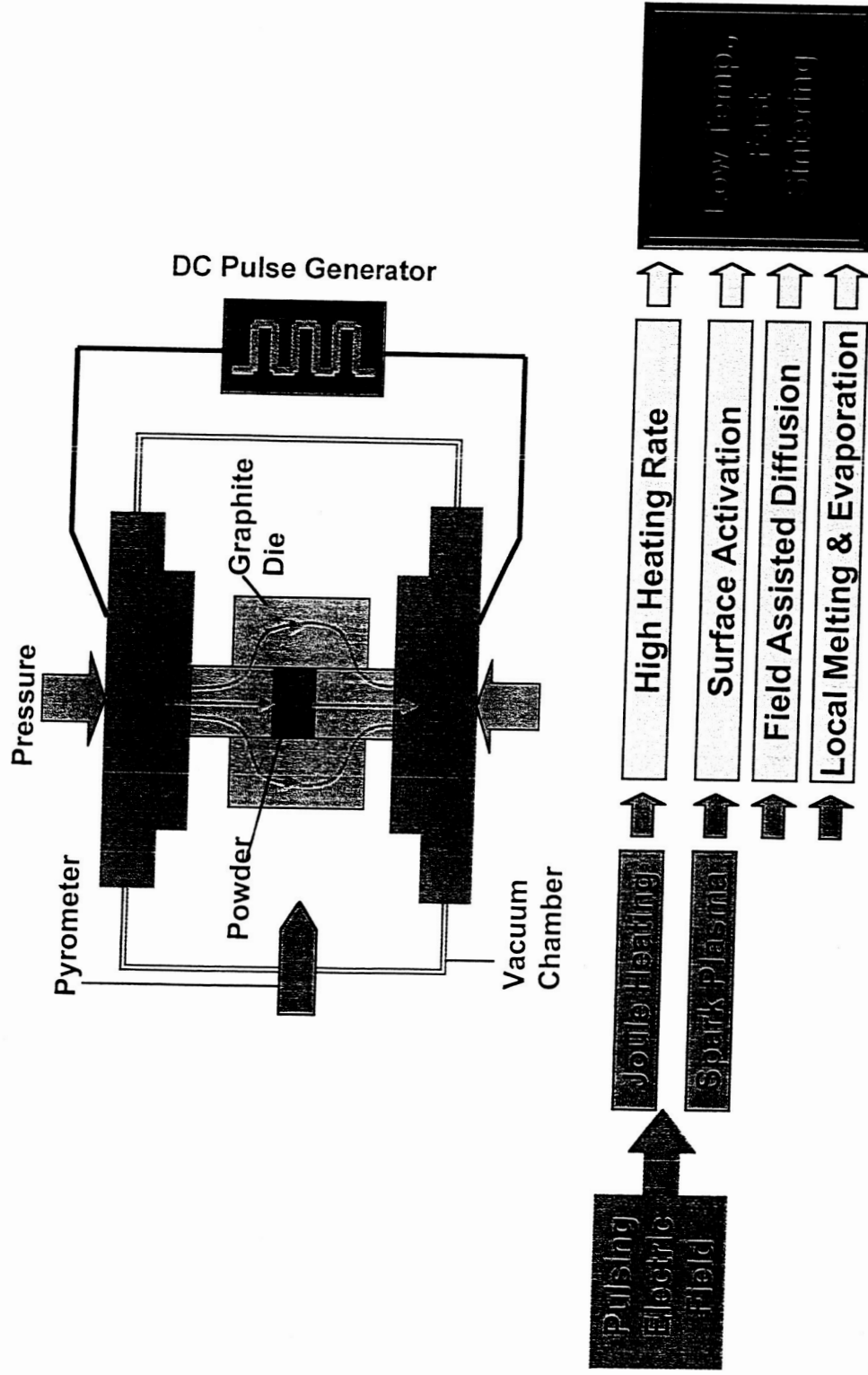
Recent Studies on the Sintering Behavior of Diboride Based Materials



Thermal Protection Materials and Systems Branch



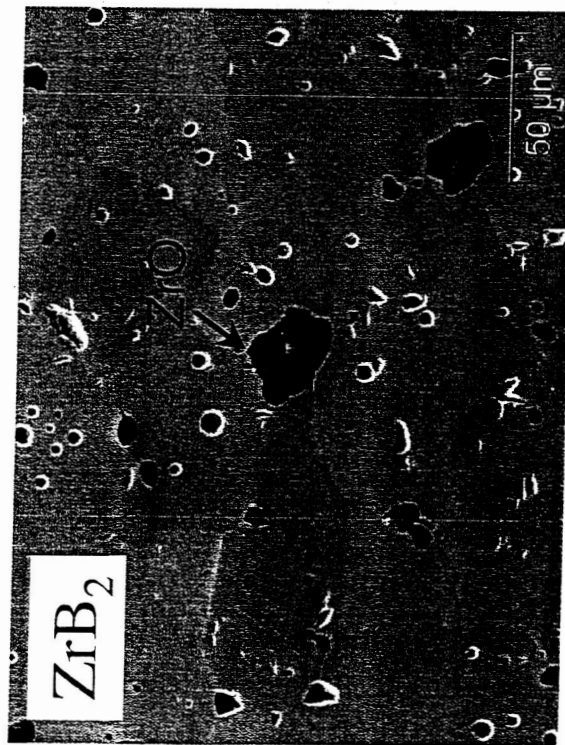
Spark Plasma Set-up





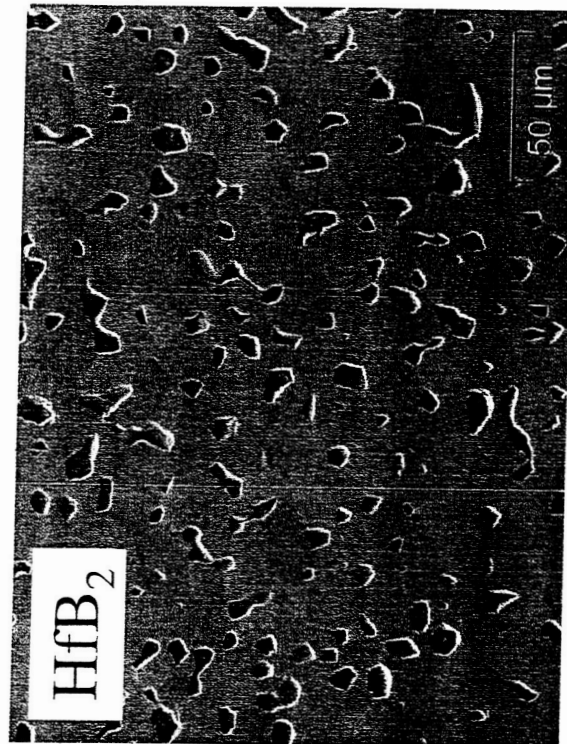
Hot Pressed - Pure Diborides

- Raw powders sinter poorly with extensive porosity when sintered at the same conditions as those materials sintered with SiC (2000-2200°C)



ZrB₂

Hot Pressed
T₁°C - 1 hour



HfB₂

Hot Pressed
T₁+200°C - 1 hour



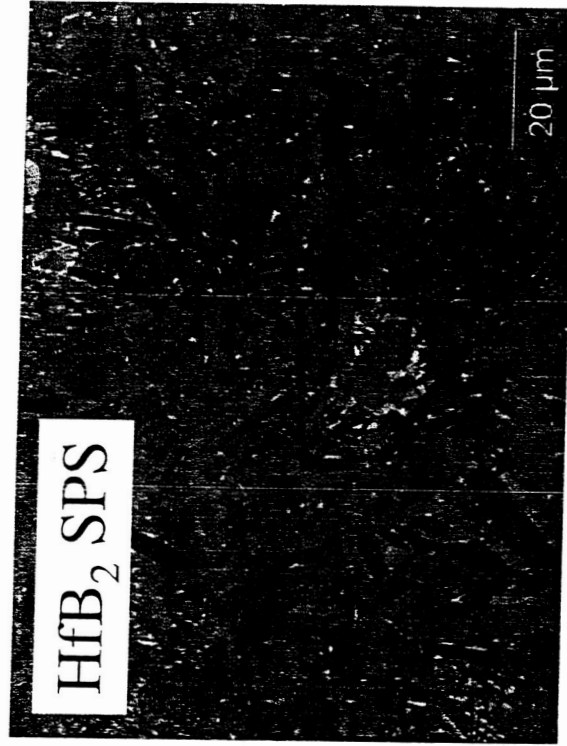
Alternatively Processed Pure HfB_2



- Hot pressed materials were porous
- SPS materials sintered with minimal porosity, reduced grain size



Hot Pressed
 $T_2^{\circ}\text{C}$ - 1 hour



Spark Plasma Sintered
 T_2 -300°C - 10 minutes





Hot Pressed - Pure Diborides

- Attempts to remove porosity by hot pressing HfB_2 and ZrB_2 at a higher temperature failed when raw powders became molten and leaked from the die.





Raw Material Processing



$\text{MOxide} + \text{B} + \text{Boron Carbide} + \text{C} \Rightarrow \text{MBoride} + \text{Side Products}$

- Typical Metal Boride reaction used is capable of yielding large quantities of powder but can contain side products (borates) or a product with off target stoichiometry



- Elemental reaction (under investigation) can yield a more stoichiometric product free from most side products
- Currently yields small quantities of powder but scalability is under investigation by our vendor, Cerac, Inc.





Other Free Sintered Borides and Carbides



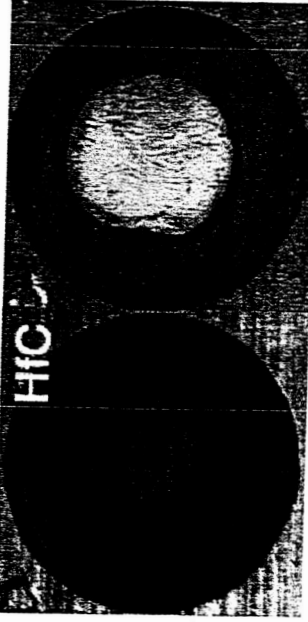
- HfB_2 formed from an elemental reaction did not melt, neither did the carbides of Hf and Zr



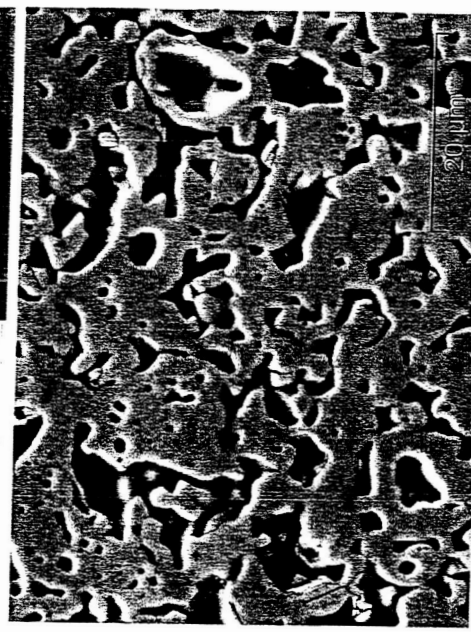
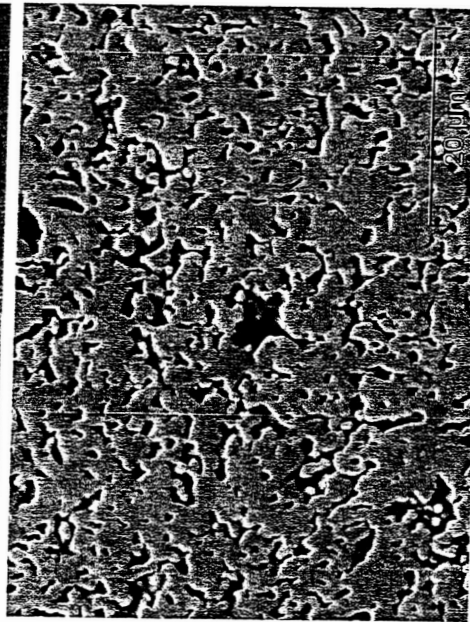
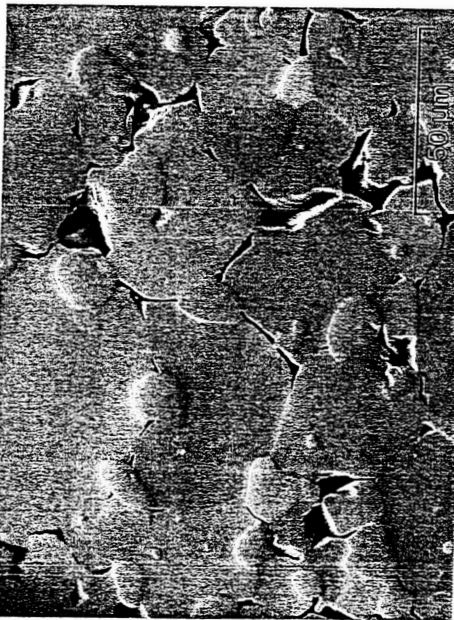
Pure HfB_2



HfC



ZrC



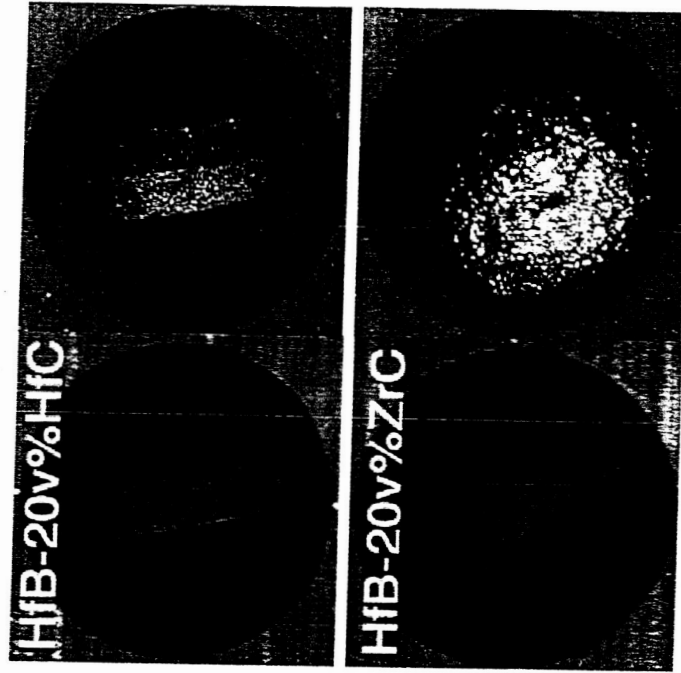
All samples Free Sintered @ 2350°C - 30 minutes



Boride / Carbide Mixtures



- Free Sintered Boride/Carbide mixtures show varied results, still under investigation



Free Sintered
2350°C - 30 minutes

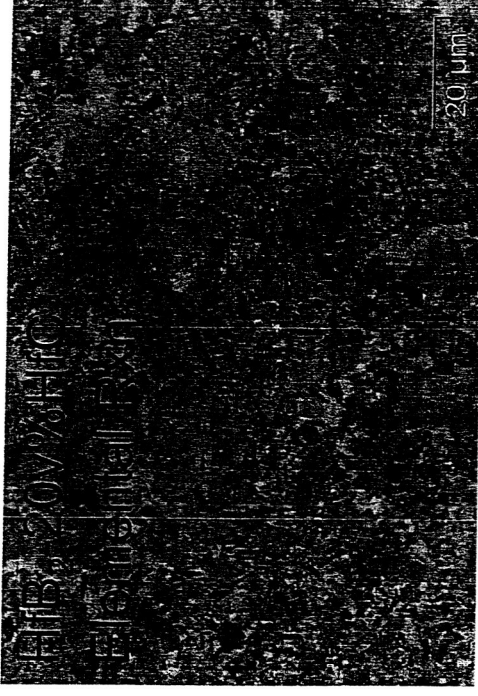




Alternatively Processed Boride / Carbide Mixtures



- Elemental reaction of Hf-B-C sinters to near full density yielding a microstructure with a even distribution of fine grains
- Compound reaction of Hf-B & ZrC does not sinter well, yielding phase separation and a porous microstructure



Spark Plasma Sintered
 T_2 -300°C - 10 minutes



Conclusions



- Raw materials do not hot press well but can be consolidated with alternate methods such as Spark Plasma Sintering.
- Increased hot press temperatures revealed that as received hafnium and zirconium diboride were found to liquefy well below their theorized melting point.
- Improvements in raw material processing and powder mixing show promising results

